Influence of long-range correlated surface and near the surface disorder on the process of adsorption of long-flexible polymer chains.

Z.Usatenko[1,2,3], J.-U. Sommer [1,4]

[1] *Leibniz Institute of Polymer Research Dresden e.V., 01069 Dresden, Germany*

[2] *Institute for Condensed Matter Physics,*

National Academy of Sciences of Ukraine, UA–79011 Lviv, Ukraine *

[3] *Marian Smoluchowski Institute of Physics,*

Jagellonian University, Department of Statistical Physics,

Reymonta 4, Kraków, Poland and

[4] *Institute for Theoretical Physics, Technische*

Universität Dresden, 01062 Dresden, Germany

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Abstract

The influence of long-range correlated surface and decaying near surface disorder with quenched defects is studied. We consider a correlation function for the defects of the form $\frac{e^{-z/\xi}}{r^a}$, where $a < d - 1$ and z being the coordinate in the direction perpendicular to the surface and r denotes the distance parallel to the surface. We investigate the process of adsorption of long-flexible polymer chains with excluded volume interactions on a "marginal" and attractive wall in the framework of renormalization group field theoretical approach up to first order of perturbation theory in a double (ϵ, δ)- expansion ($\epsilon = 4 - d$, $\delta = 3 - a$) for the semi-infinite $|\phi|^4$ $O(m, n)$ model with the above mentioned type of surface and near the surface disorder in the limit $m, n \to 0$. In particular we study two limiting cases. First, we investigate the scenario where the chain's extension it much larger then ξ. Second, we consider the case where the chain's extension is of the order of ξ. For both cases we obtained series for bulk and the whole set of surface critical exponents, characterizing the process of adsorption of long-flexible polymer chains at the surface. The polymer linear dimensions parallel and perpendicular to the surface and the corresponding partition functions as well as the behavior of monomer density profiles and the fraction of adsorbed monomers at the surface and in the volume are studied.

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*Electronic address: `zz_usatenko&ph.icmp.lviv.ua`

I. INTRODUCTION

Adsorption and localization processes of macromolecules are very important for polymer technology in many areas such as lubrication, adhesion, surface protection or compact disc production. Investigation of adsorption phenomena allows to understand biological processes of polymer-membrane interactions as well as such processes of biotechnology as DNA micro-arrays and electrophoresis. Therefore, the statistical properties of the adsorption of long, flexible macromolecular chains (polymers) at surfaces in dilute, semi-dilute, and concentrated polymer solutions have found considerable interest [1–3].

Generally, a thorough theoretical understanding of the statistical physics of polymers can be reached using well developed mathematical tools from field theory. Long flexible polymer chains immersed into a good solvent are very well described by the model of self-avoiding walks (SAWs) on a regular lattice [4, 5]. As revealed by de Gennes, the conformations of a SAW exhibit critical (self-similar) behavior approaching the limit of infinite number of steps which can be extracted from the $m \to 0$ limit of an $O(m)$ symmetric field theory (polymer-magnet analogy) [6]. Using this intimate relation with critical phenomena, polymers in the bulk phase have been extensively studied in the past, and many of their properties could be clarified [5]. On the other hand, the theory of surface critical phenomena in such complex systems has many facets and is still far from being complete. This concerns in particular adsorption and localization phenomena at surfaces and interfaces, as well as the influence of different kinds of disorder effects which naturally occur in many polymer environments, including structured surfaces.

As noted already by de Gennes [6] and by Barber et al. [7], there is a formal analogy of the polymer adsorption problem to the equivalent problem of critical phenomena in the semi-infinite $|\phi|^4$ n-vector model of a magnet with a free surface [8, 9]. In this case any bulk universality class is split into several surface universality classes, with new surface critical exponents [8, 9]. It should be mentioned that such analogy takes place for a real polymer chain, i.e., polymers with excluded volume interaction. Based on the polymer-magnet analogy, the problem of adsorption of flexible polymer chains on a surface in the case of good solvent without disorder was investigated few years ago by Eisenriegler and co-workers [1, 10, 11]. Besides, the adsorption transition of linear polymers was subject of a series of recent works, see [12–17].

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Real systems usually contain some geometric surface defects and impurities both on the substrate and within the bulk. On the other hand, disorder effects on surfaces can become interesting for separation of polymers (electrophoresis on chip) [18, 19], or very general in the context of nano-structured surfaces and biological systems such as cell membranes.

It has been shown that quenched short-range correlated bulk disorder does not alter the polymer bulk critical exponents [20, 21]. However, the asymptotic behavior of polymers in media with *long-range correlated disorder* is characterized by a new set of bulk critical exponents [22, 23].

In our recent work [24] we have extended previous studies to investigate the influence of long-range correlated bulk disorder on the process of adsorption of long flexible polymer chains from solution onto a planar surface forming the system boundary. Our investigations have shown that the system with long-range correlated bulk disorder is characterized by a new set of surface critical exponents, and belongs to a new universality class ("long-range" fixed point). Our results show that a larger range of correlations between the defects enhances the trapping of the chain between the attractive surface on one side, and the region occupied by the defects on the other side. Thus, the fraction of the monomers near the wall can be higher than right at the wall.

Introducing into the system *short-range correlated surface disorder* only turns out to be irrelevant for surface critical behavior [25–27]. On the other hand, long-range correlated surface disorder with a correlation function given by $g(r) \sim 1/r^a$, where r denotes the distance in the direction parallel to the surface, can be relevant for the asymptotic behavior of polymer adsorption if $a < d - 1$; but it turns out to be irrelevant if $a \geq d - 1$, as was suggested in Ref.[25]. However, there remain some points to clarify, such as a detailed analysis of the surface critical behavior of the systems with long-range correlated surface disorder and the calculation of surface critical exponents.

In the present work we investigate the influence of quenched long-range correlated disorder in the direction parallel to the surface and decaying with a finite correlation length ξ in the direction perpendicular to the surface. In particular, we consider such type of disorder with quenched defects obeying by a following law of correlation :

$$g(x) = \frac{e^{-z/\xi}}{r^a} \quad , \tag{1}$$

where z denotes the distance between two points in the direction perpendicular to the surface,

and r denotes the distance between two points in the direction parallel to the surface. Adsorption of flexible chains is considered on impenetrable surfaces, with $z \geq 0$, in the "marginal" and attractive region of polymer surface interactions. The model is sketched in Fig.1. Impurities block surface sites for polymer adsorption as well as bulk sites. Long range correlated disorder in the direction parallel to the surface can occur due to agglomeration or percolation effects of the impurities. The correlation disappears over a typical length scale of ξ in the direction perpendicular to the surface. We hasten to note that the correlation function given in Eq.(1) implies also a layer-like structure of the impurities in the bulk.

In order to investigate the critical behaviour of the semi-infinite $|\phi|^4$ $O(m, n)$ model with above mentioned correlated disorder in the limit $m, n \to 0$ we apply the renormalization group (RG) field theoretical approach and choose the massive field theory scheme with renormalization at non-zero mass and zero external momenta [46]. For the quantative analysis of the first order results we apply the double (ϵ, δ)- expansion. But it is necessary to add that in our case we use $\epsilon = 4 - d$, $\delta = 3 - a$ expansion in contrast to $\epsilon = 4 - d$, $\delta = 4 - a$ expansion proposed by Weinrib and Halperin [39]. The choice of expansion in δ is connected in natural way with the value of a that in our case of surface and near the surface disorder is $a < d - 1$.

The analysis of the obtained series for the surface critical exponents, characterizing the process of adsorption of long-flexible polymer chains at the surface is performed. The polymer linear dimensions parallel and perpendicular to the surface and the corresponding partition functions as well as the scaling behavior of monomer density profiles and the fraction of adsorbed monomers at the surface and close to the surface are studied.

II.   THE MODEL

In this work we investigate the adsorption phenomena of long, flexible linear polymer chains at a "marginal" and attractive surface in sufficiently diluted polymeric solution so that inter-chain interactions in the bulk and on the surface can be neglected. In this case the full information about the process of adsorption of polymer chains at the surface is obtained by considering the configurations of a single chain.

Let us consider a polymer solution in contact with a solid substrate where the monomers in contact with the surface gain energy (attractive surface). Such is usually realized by Van-

der-Waals interactions between the monomers and the substrate. In polarizable polymer-surface systems also stronger interactions such as hydrogen-bonds can occur. Here, we will consider the case of monomer-surface interactions which shall be of the order of kT (k Boltzmann constant, T absolute temperature). This is usually referred to as weak or reversible adsorption. By contrast, interaction energies much larger than kT lead to quasi-irreversible adsorption processes which require non-equilibrium models. Also for weak adsorption at sufficiently low temperatures, $T < T_a$, an adsorbed state of the chains is caused by the dominance of surface interactions over the conformational entropy of free chains, where a finite fraction of the monomers is localized at the system boundary. This leads to an interesting transition phenomenon where the polymer chain conformations changes from an isotropic state to a highly anisotropic "pancake-like" state.

The deviation from the adsorption threshold introduced above, $c \propto (T - T_a)/T_a$, changes sign at the transition between the adsorbed ($c < 0$) and the non-adsorbed state ($c > 0$) and it plays a role of a second critical parameter. The value $1/N$, where N is a number of monomers, plays a role of the primary critical parameter analogous to the reduced critical temperature in magnetic systems. Thus, the adsorption threshold for infinite polymer chains, where $1/N \to 0$ and $c = c_0^{sp} \to 0$ is a multicritical phenomenon. For ($T > T_a$) the so-called ordinary transition corresponds to a "repulsive surface" and the limit $1/N \to 0$ leads to usual bulk behavior. The case $T < T_a$ corresponds to the "attractive surface" at which a surface state occurs. Both regions are joint by the multicritical point which corresponds to a "marginal" surface state at $T = T_a$. The limit $1/N \to 0$ at $c = 0$ is referred to as the *special transition.* As it is known [8, 30], for each of these regions in the parameter space the knowledge of one independent surface critical exponent gives access to the whole set of the other surface critical exponents via surface scaling relations and the bulk critical exponents ν and η. An example being the critical exponent $\eta_\parallel$ which is related to chain correlations in directions parallel to the surface.

Of particular importance for polymer adsorption phenomena is the so-called crossover exponent Φ. The knowledge of Φ allows to describe the crossover behavior between the special and ordinary transitions ($c \neq 0$). The exponent Φ is related to the length scale ξ_c [1, 11] given by

$$\xi_c \sim |c|^{-\nu/\Phi} \quad , \tag{2}$$

associated with the parameter c. In the polymer problem the length scale ξ_c can be inter-

preted as the distance from the surface up to which the properties of polymer chains depend on the value of c, not only on its sign. In the case of adsorption ξ_c defines the extension of the chain in the direction perpendicular to the surface (blob size). In the bulk the relevant length scale is the average end-to-end distance

$$\xi_R = \sqrt{<R^2>} \sim N^\nu \quad . \tag{3}$$

Additionally, there is the microscopic length l – the statistical segment length which denotes the limit of validity of the corresponding coarse grained model. Near the multicritical point the only relevant length scales are $\xi_R \to \infty$ and $\xi_c \to \infty$. Correspondingly, the properties of the system depend on the ratio ξ_R/ξ_c. The characteristic ratio is $(\xi_R/\xi_c)^{\Phi/\nu} \sim |c|N^\Phi$, where cN^Φ is the scaling variable controling weak adsorption of polymers[10]. On the other hand, Φ can be related to the number of monomers in contact to the surface, N_1, at T_a according to $N_1 \sim N^\Phi$, as well as with the density profile within the chain at T_a. There is some dispute about the correct value of Φ [10, 30–32] for homopolymer chains at pure surfaces. In a recent work, we have shown that more reliable results for critical exponents characterizing the process of adsorption of long-flexible polymer chains can be obtained in the frames of massive field-theory approach directly at three dimensions [34].

The description of the surface critical behavior of long-flexible polymer chains near the wall can be formulated in terms of the effective Landau-Ginzburg-Wilson (LGW) Hamiltonian of the semi-infinite m-vector model [9, 35]

$$H = \int_V d^d x [\frac{1}{2} \mid \nabla \vec{\phi} \mid^2 + \frac{1}{2}\bar{\mu}_0{}^2 \mid \vec{\phi} \mid^2 + \frac{1}{4!}v_0(\vec{\phi}^2)^2] + \frac{c_0}{2} \int_{\partial V} d^{d-1} r \vec{\phi}^2(\mathbf{r}, z = 0) \quad , \tag{4}$$

where $\vec{\phi}(x)$ is an m-vector field with the components $\phi_i(x)$, $i = 1, ..., m$. It should be mentioned that the d-dimensional spatial integration is extended over a half-space $V = I\!R^d_+ \equiv \{\mathbf{x}=(\mathbf{r}, z) \in I\!R^d \mid \mathbf{r} \in I\!R^{d-1}, z \geq 0\}$ bounded by a plane free surface ∂V at $z = 0$. Here $\bar{\mu}_0{}^2$ is the "mass", v_0 denotes the coupling constant of the model (excluded volume for polymer chains) and c_0 describes the surface-enhancement of the interactions.

Inhomogeneities or defects in the system cause local deviations from the average value of the transition temperature. This has been shown in the experiments on Gd [36–38]. According to the consideration above, one of the possibilities to introduce disorder effects into the model is to assume that the parameter $\bar{\mu}_0$ incorporates *local random temperature*

fluctuations $\delta\tau(x)$ via $\bar{\mu}_0 = \mu_0 + \delta\tau(x)$. The value $\delta\tau(\mathbf{x})$ represents the quenched random-temperature disorder, with $< \delta\tau(\mathbf{x}) >= 0$ and

$$\frac{1}{8} < \delta\tau(\mathbf{x})\delta\tau(\mathbf{x}') >= g(|\mathbf{x} - \mathbf{x}'|), \tag{5}$$

where angular brackets $< ... >$ denote configurational averaging over quenched disorder. By analogy with the isotropic pair correlation function as was introduced by Weinrib and Halperin [39], we choose the pair correlation function with anisotropy of disorder in the direction parallel and perpendicular to the surface in the form Eq.(1). The presence of the surface restricts translational invariance to translations parallel to the surface. Thus, we introduce the Fourier-transform $\tilde{g}(\mathbf{q}, z)$ of $g(\mathbf{x})$ only in the direction parallel to the surface. Using Eq.(1), we obtain

$$\tilde{g}(\mathbf{q}, z) \sim u_0 + w_0 \mid \mathbf{q} \mid^{a-d+1} e^{-z/\xi}. \tag{6}$$

Applied to Eq.(5) this corresponds to the so-called long-range correlated "random-temperature" surface and decaying near the surface disorder. In the case of random uncorrelated point-like (or short-range correlated) surface disorder the site-occupation correlation function is $g(r) \sim \delta(r)$ and its Fourier-transform assumes the simple form $\tilde{g}(q) \sim u_0$. As was shown in [25], short-range correlated (or random uncorrelated point-like) surface and short-range correlated bulk disorder [21] are irrelevant for surface critical behavior. In these cases in the limit $m, n \to 0$ the u_0 and v_0 terms have the same symmetry, and we pass to an effective Hamiltonian with only one coupling constant $V_0 = v_0 - u_0$. We keep the notation v_0 for the coupling V_0.

By contrast, taken into account Eq.(6), the long-range correlated surface and near the surface disorder can be relevant for SAW's, because the w_0 term is relevant in the renormalization group sense if $a < d - 1$. If $a \geq d - 1$ the w_0 term is irrelevant and one obtains the effective Hamiltonian of the system with random uncorrelated point-like disorder.

Employing the replica trick to carry out averages over different configurations of the quenched disorder, as it was first explicitly done in the RG calculations by Grinstein and Luther [40], it is possible to construct the effective Hamiltonian of the semi-infinite $|\phi|^4$ $O(m, n)$ model with a long-range correlated surface and decaying near the surface disorder

$$H_{eff} = \sum_{\alpha=1}^{n} \int_V d^d x \left[\frac{1}{2} \mid \nabla \vec{\phi}_\alpha \mid^2 + \frac{1}{2}\mu_0^2 \vec{\phi}_\alpha^2 + \frac{1}{4!}v_0(\vec{\phi}_\alpha^2)^2\right]$$

$$- \sum_{\alpha,\beta=1}^{n} \int d^d x_1 d^d x_2 g(\mid \mathbf{r}_1 - \mathbf{r}_2 \mid, z_2 - z_1)\vec{\phi}_\alpha^2(\mathbf{r}_1, z_1)\vec{\phi}_\beta^2(\mathbf{r}_2, z_2)$$

$$+ \frac{c_0}{2} \sum_{\alpha=1}^{n} \int_{\partial V} d^{d-1}r \vec{\phi}_\alpha^2(\mathbf{r}, z=0) \quad . \tag{7}$$

Here Greek indices denote replicas, and the replica limit $n \to 0$ is implied. The limit $m, n \to 0$ of this model describes the adsorption of long-flexible polymer chains interacting with a solid substrate in the presence of correlated defects or impurities. The fields $\phi_i(\mathbf{r}, z)$ satisfy the Dirichlet boundary condition in the case of ordinary transition (the case of repulsive wall): $\phi_i(\mathbf{r}, z) = 0$ at $z = 0$ and, the von Neumann boundary condition in the case of special transition (the case of "marginal" surface at the adsorption threshold): $\partial_z \phi_i(\mathbf{r}, z) = 0$ at $z = 0$ [8, 41]. The model defined in Eq.(7) is restricted to translations parallel to the boundary surface, $z = 0$.

III. SURFACE CRITICAL BEHAVIOR NEAR THE ADSORPTION THRESHOLD (FIXED POINT $c_0 = c_0^{ads}$)

A. Correlation functions and renormalization conditions

Correlation functions which involves N' fields $\phi(\mathbf{x}_i)$ at distinct points $\mathbf{x}_i(1 \le i \le N')$ in the bulk, M' fields $\phi(\mathbf{r}_j, z = 0) \equiv \phi_s(\mathbf{r}_j)$ at distinct points on the wall with parallel coordinates $\mathbf{r}_j(1 \le j \le M')$, and L insertion of the bulk operator $\frac{1}{2}\phi^2(\mathbf{X}_k)$ at points $\mathbf{X}_k$ with $1 \le k \le L$, L_1 insertions of the surface operator $\frac{1}{2}\phi_s^2(\mathbf{R}_l)$ at points $\mathbf{R}_l$ with $1 \le l \le L_1$, have the form [9, 30]

$$G^{(N',M',L,L_1)}(\{\mathbf{x}_i\}, \{\mathbf{r}_j\}, \{\mathbf{X}_k\}, \{\mathbf{R}_l\}) = < \prod_{i=1}^{N'} \phi(\mathbf{x}_i) \prod_{j=1}^{M'} \phi_s(\mathbf{r}_j) \prod_{k=1}^{L} \frac{1}{2}\phi^2(\mathbf{X}_k) \prod_{l=1}^{L_1} \frac{1}{2}\phi_s^2(\mathbf{R}_l) > \quad . \tag{8}$$

Here, $< ... >$ denotes averaging with the Boltzmann factor, where the Hamiltonian is given in Eq.(7). The full free propagator of a Gaussian chain in *semi-infinite space* in the

mixed $\mathbf{p}, z$ representation is given by [9]

$$G_0(\mathbf{p}, z', z) = \frac{1}{2\kappa_0} \left[e^{-\kappa_0|z'-z|} - \frac{c_0 - \kappa_0}{c_0 + \kappa_0} e^{-\kappa_0(z'+z)} \right], \tag{9}$$

where $\kappa_0 = \sqrt{p^2 + \mu_0^2}$ and $\mathbf{p}$ denotes the Fourier transform for the Cartesian components parallel to the surface.

Taking into account that surface fields $\phi_s(\mathbf{r})$ and surface operators $\frac{1}{2}\phi_s^2(\mathbf{R})$ scale with scaling dimensions that are different from those of their bulk analogs $\phi(\mathbf{x})$ and $\frac{1}{2}\phi^2(\mathbf{X})$ (see [30]), the renormalized correlation function involving N' bulk fields and M' surface fields and L bulk operators, L_1 surface operators can be written as

$$G_R^{(N',M',L,L_1)}(\mathbf{p}; \mu, v, w, c) = Z_\phi^{-(N'+M')/2} Z_1^{-M'/2} Z_{\phi^2}^L Z_{\phi_s^2}^{L_1} G^{(N',M',L,L_1)}(\mathbf{p}; \mu_0, v_0, w_0, c_0), \tag{10}$$

where Z_ϕ, Z_1 and Z_{ϕ^2}, $Z_{\phi_s^2}$ are correspondent UV-finite ($d < 4$) renormalization factors. The typical bulk and surface short-distance singularities of the correlation functions $G^{(N',M')}$ are removed via mass shift $\mu_0^2 = \mu^2 + \delta\mu^2$ and surface enhancement shift $c_0 = c + \delta c$, respectively (see Ref. [30]).

The renormalized mass μ, coupling constants v, w, and the renormalization factor Z_ϕ, Z_{ϕ^2} are fixed formally via the standard normalization conditions of the infinite-volume theory [40, 42–44]

$$\Gamma^{(2)}{}_{b,R}(q, v, w, \mu) \mid_{q=0} = \mu^2,$$

$$\Gamma^{(4)}{}_{v,R}(\{q_i\}, v, w, \mu) \mid_{\{q_i\}=0} = \mu^\epsilon v,$$

$$\Gamma^{(4)}{}_{w,R}(\{q_i\}, v, w, \mu) \mid_{\{q_i\}=0} = \mu^\delta w,$$

$$\frac{\partial}{\partial q^2}\Gamma^{(2)}{}_{b,R}(q, \mu, v, w) = 1,$$

$$\Gamma^{(2,1)}{}_{b,R}(\{\mathbf{q}\}, \{\mathbf{Q}\}, \mu, v, w,) \mid_{\{\mathbf{q}=\mathbf{Q}=0\}} = 1, \tag{11}$$

with $\epsilon = 4 - d$ and $\delta = 3 - a$. The renormalized vertex function is given by

$$\Gamma_{b,R}^{(N',L)}(\{q_i, Q_i\}, \mu, v, w) = [Z_\phi]^{N'/2}[Z_{\phi^2}]^L \Gamma_b^{(N',L)}(\{q_i, Q_i\}, \mu_0, v_0, w_0). \tag{12}$$

Thus, taking into account the normalization conditions, Eq.(11), we can remove the typical bulk short-distance singularities of the correlation function after performing the mass renormalization

$$\mu_0^2 = (Z_\phi)^{-1}\mu^2 - \frac{v_0}{3}J_1(\mu) + \frac{w_0}{3}J_2(\mu), \tag{13}$$

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with

$$J_1(\mu) = \frac{1}{(2\pi)^{d-1}} \int \frac{d^{d-1}q}{2\kappa_q},$$

$$J_2(\mu) = \frac{1}{(2\pi)^{d-1}} \int d^{d-1}q \frac{|q|^{a-d+1}}{2\kappa_q(\frac{1}{\xi} + \kappa_q)}, \tag{14}$$

where $\kappa_q = \sqrt{q^2 + \mu^2}$. In order to remove short-distance singularities of the correlation function $G^{(N',M')}$ located in the vicinity of the surface, the surface-enhancement shift $c_0 = c + \delta c$ is required. The required surface normalization conditions are (see [30])

$$G_R^{(0,2)}(0; \mu, v, w, c) = \frac{1}{\mu + c} \tag{15}$$

and

$$\left. \frac{\partial G_R^{(0,2)}(p; \mu, v, w, c)}{\partial p^2} \right|_{p=0} = -\frac{1}{2\mu(\mu + c)^2}, \tag{16}$$

$$\left. G_R^{(0,2,0,1)}(\mathbf{p}; \mu, v, w, c) \right|_{\mathbf{p}=0} = \frac{1}{(\mu + c)^2} \tag{17}$$

Equation (15) defines the surface-enhancement shift δc and shows that the surface susceptibility diverge at $\mu = c = 0$. This point corresponds to the multicritical point (μ_{0c}^2, c_0^{ads}) at which adsorption threshold takes place. The normalization condition of Eq. (9) and the expression for the renormalized correlation function of Eq. (10), allow to find the renormalization factor $Z_\| = Z_1 Z_\phi$ from the relation

$$Z_\|(v, w)^{-1} = 2\mu \frac{\partial}{\partial p^2}[G^{(0,2)}(p)]^{-1} \bigg|_{p^2=0} = \lim_{p \to 0} \frac{\mu}{p} \frac{\partial}{\partial p}[G^{(0,2)}(p)]^{-1}. \tag{18}$$

The Eq.(17) allows to obtain the renormalization factor $Z_{\phi_s^2}$ from

$$[Z_{\phi_s^2}(v, w)]^{-1} = Z_\| \frac{\partial[G^{(0,2)}(0; \mu_0, v_0, w_0, c_0)]^{-1}}{\partial c_0} \bigg|_{c_0=c_0(c,\mu,v,w)}, \tag{19}$$

where relation $G^{(0,2;0,1)}(0; \mu_0, v_0, w_0, c_0) = -(\frac{\partial}{\partial c_0})G^{(0,2)}(0; \mu_0, v_0, w_0, c_0)$ have been taken into account.

B. Analysis of Callan-Symanzik equations

Asymptotically close to the critical point (μ_{0c}^2, c_0^{ads}) the renormalized correlation functions $G^{(0,2)}$ satisfy the homogeneous Callan-Symanzik (CS) equations [45–47] with the

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corresponding renormalization group (RG) functions. The first part of these RG functions are β-functions $\beta_v(v,w) = \mu \frac{\partial}{\partial \mu}\big|_0 v$, $\beta_w(v,w) = \mu \frac{\partial}{\partial \mu}\big|_0 w$, and usual bulk exponent $\eta = \mu \frac{\partial}{\partial \mu}\big|_0 \ln Z_\phi$. The second part of these RG functions is a surface-related function

$$\eta_1^{sp}(v,w) = \mu \frac{\partial}{\partial \mu}\bigg|_0 \ln Z_1(v,w). \tag{20}$$

In the case of investigation the crossover behavior from the adsorbed to the non-adsorbed states (see [24, 30, 48]) the additional surface related term arises $-[1 + \eta_{\bar{c}}(v,w)]\bar{c}\frac{\partial}{\partial \bar{c}}$, with crossover-related function

$$\eta_{\bar{c}}(v,w) = \mu \frac{\partial}{\partial \mu}\bigg|_0 \ln Z_{\phi_s^2}(v,w), \tag{21}$$

where $\big|_0$ indicates that the derivatives are taken at fixed cutoff Λ, fixed bare coupling constants and surface enhancement constant.

The simple scaling dimensional analysis of $G_R^{(0,2)}$ and of the mass dependence of the Z factors, allows to express the surface correlation exponent $\eta_\parallel^{sp}$ which characterizes the critical point correlations parallel to the surface as

$$\eta_\parallel^{sp} = \eta_1^{sp} + \eta. \tag{22}$$

Taking into account Eqs. (18), (20) and (22), the surface correlation exponent $\eta_\parallel^{sp}$ is presented via the following expression

$$\begin{aligned} \eta_\parallel^{sp} &= \mu \frac{\partial}{\partial \mu}\bigg|_0 \ln Z_\parallel \\ &= \beta_v(v,w)\frac{\partial \ln Z_\parallel(v,w)}{\partial v} + \beta_w(v,w)\frac{\partial \ln Z_\parallel(v,w)}{\partial w}\bigg|_{FP}. \end{aligned} \tag{23}$$

Here FP is a notation of the corresponding fixed point. It should be mentioned that in the current case the nontrivial long-range (LR) fixed point is present, which becomes stable when some amount of long-range correlated surface and near the surface disorder with $a < d - 1$ is introduced into the system.

Taking into account (21), the crossover-related function $\eta_{\bar{c}}(v,w)$ can be written as

$$\eta_{\bar{c}}(v,w) = \beta_v(v,w)\frac{\partial \ln Z_{\phi_s^2}(v,w)}{\partial v} + \beta_w(v,w)\frac{\partial \ln Z_{\phi_s^2}(v,w)}{\partial w}\bigg|_{FP}. \tag{24}$$

The asymptotic scaling critical behavior of the correlation functions near the multicritical point can be obtained through a detailed analysis of the CS equations, as was proposed in Ref. [45, 49] and employed in the case of the semi-infinite systems in [24, 30, 48, 50, 51].

Using the above mentioned scheme, the asymptotic scaling form of the surface correlation functions of the long-flexible polymer chains with one end fixed at the surface and the other end is located somewhere in the layer z above the surface can be written as

$$G^\lambda(z, c_0) \sim z^{1-\eta_\perp^{sp}} G_\lambda(\tau z^{1/\nu}, \tau^{-\Phi}\Delta c_0) \ . \tag{25}$$

Similarly, for chains with both ends fixed on the surface at distance r, or for chains with only one end fixed on the surface and $r_A = r_B$, we can write

$$G^{\|,\perp}(x; c_0) \sim x^{-(d-2+\eta_{\|,\perp}^{sp})} G_{\|,\perp}(\tau x^{1/\nu}; \tau^{-\Phi}\Delta c_0), \tag{26}$$

where $\eta_\perp^{sp} = \frac{\eta+\eta_\|^{sp}}{2}$ is the surface critical exponent which characterizes the critical point correlations perpendicular to the surface; $\Phi = \nu(1+\eta_{\bar{c}}(v^*, w^*))$ is the surface crossover critical exponent [24, 30, 48], which characterizes the measure of deviation from the multicritical point and x denotes r or z in $G^\|$ or $G^\perp$, which correspond to $G^{(0,2)}$ and $G^{(1,1)}$ functions, respectively.

IV. ONE-LOOP APPROXIMATION RESULTS

In general, there are two possibilities to investigate the critical behavior of the model. In the first scheme one considers correspondent polynomials for β-functions and renormalization factors as functions of renormalized coupling constants v, w for fixed d, a. Then one searches for stable solutions of the fixed point equations. The corresponding one-loop equations in this case do not have any stable accessible fixed points for $d < 4$. In order to obtain reasonable results within this scheme the knowledge of the second order of perturbation theory is required. There exists a second scheme to perform the quantitative analysis of the first order results which implies a double expansion in $\epsilon = 4 - d$ and $\delta = 3 - a$ (with $a < d - 1$) by analogy as was proposed by Weinrib and Halperin [39]. But, it should be mentioned that in our case of long-range correlated surface and decaying near the surface disorder the upper critical dimension for the correlation parameter of disorder a is $d_a = 3$ in contrast to the case of system with long-range correlated bulk disorder, where $d_a = 4$. We we use the second approach in our investigations of adsorption of long-flexible polymer chains with excluded volume interactions on the surface with long-range correlated surface and decaying near the surface disorder.

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After performing the integration of the corresponding Feynman diagrams, for the bulk renormalization factors Z_ϕ and Z_{ϕ^2} at the first order of perturbation theory, we obtain

$$
\begin{aligned}
Z_\phi(\bar{v}, \bar{w}) &= 1 + \frac{\bar{w}}{3} I_4, \\
Z_{\phi^2}(\bar{v}, \bar{w}) &= 1 + \frac{\bar{v}}{3} + \frac{\bar{w}}{3}(I_5 - I_4),
\end{aligned}
\tag{27}
$$

where the following definitions for the correspondent integrals were introduced

$$
\begin{aligned}
I_4 &= -(I_1\xi)^{-1}\frac{1}{(2\pi)^d}\frac{\partial}{\partial k_1^2}\int d^dk \frac{|q|^{a-d+1}}{(k_1+k)^2+1}\int_0^\infty dz e^{ifz}e^{-|z|/\xi}, \\
I_5 &= -(I_1\xi)^{-1}\mu^\delta\frac{1}{(2\pi)^d}\frac{\partial}{\partial \mu^2}\int d^dk \frac{|q|^{a-d+1}}{(k_1+k)^2+\mu^2}\int_0^\infty dz e^{ifz}e^{-|z|/\xi},
\end{aligned}
\tag{28}
$$

with

$$
I_1 = \frac{1}{(2\pi)^d}\int \frac{d^dk}{(k^2+1)^2} = \pi^{-d/2}2^{-d}\Gamma(2-\frac{d}{2})
$$

and $\mathbf{k} = (\mathbf{q}, f)$, where $\mathbf{q}$ is $d-1$ dimensional vector of momenta. The rescaled renormalized coupling constants $\bar{v}, \bar{w}$ are introduced as follows $\bar{v} = vI_1$, $\bar{w} = wI_1$. Besides, the vertex renormalization of the bare parameters in the present case of calculation at first order according to Eq.(11) are $v_0 = v\mu^\epsilon$ and $-w_0\xi = w\mu^\delta$ with $\epsilon = 4-d$ and $\delta = 3-a$, respectively. It should be mentioned, that in the present case of anisotropy of disorder in the direction parallel and perpendicular to the surface we distinguished integration in direction parallel and perpendicular to the surface. By the complexity of the initial form of the correlation function characterizing disorder (see Eq.(1)), the contributions from parallel momenta $\mathbf{q}$ and perpendicular momenta f are interconnected which each other. The correspondent β-functions has a form

$$
\begin{aligned}
\beta_{\bar{v}}(\bar{v}, \bar{w}) &= -\epsilon\bar{v}(1-\frac{4}{3}\bar{v}) + 2\delta\bar{v}\bar{w}(I_2-\frac{I_4}{3}) + \frac{2}{3}\bar{w}^2 I_3(2\delta-\epsilon), \\
\beta_{\bar{w}}(\bar{v}, \bar{w}) &= -\delta\bar{w} + \frac{2}{3}\bar{v}\bar{w}\epsilon + \frac{2}{3}\delta\bar{w}^2(I_2-I_4),
\end{aligned}
\tag{29}
$$

where we have introduced the following definitions

$$
\begin{aligned}
I_2 &= (I_1\xi)^{-1}\frac{1}{(2\pi)^d}\int d^dk \frac{|q|^{a-d+1}}{((k_1+k)^2+1)^2}\int_0^\infty dz e^{ifz}e^{-|z|/\xi}, \\
I_3 &= (I_1\xi)^{-1}\frac{1}{(2\pi)^d}\int d^dk \frac{|q|^{2(a-d+1)}}{((k_1+k)^2+1)^2}\int_0^\infty dz e^{ifz}e^{-2|z|/\xi}.
\end{aligned}
\tag{30}
$$

Taking into account (27) and correspondent order of β-functions we obtain one-loop order

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results for the bulk critical exponents ν and η

$$\nu = \frac{1}{2} + \frac{\epsilon \bar{v}}{12} + \frac{\delta \bar{w}}{12}(I_5 - I_4),$$
$$\eta = -\frac{\bar{w}\delta}{3}I_4. \tag{31}$$

In our calculations we distinguish two cases: near the surface disorder $\xi << \xi_R$ and the case of extended disorder on the distance of the correlation length ξ_R, i.e. $\xi \sim \xi_R$.

A.   The case of near the surface disorder $\xi << \xi_R$

First of all discuss the situation of near the surface disorder, i.e. the case $\xi << \xi_R$.

After performing double (ϵ, δ) - expansion of the above mentioned integrals Eq.(28) and Eq.(30), we obtain

$$I_4 =\sim \frac{(\delta - \epsilon)\epsilon}{2\delta^2 \pi^{\frac{d}{2}+1}}, \qquad I_5 =\sim \frac{(1-\delta)\epsilon}{\delta}, \tag{32}$$

and

$$I_2 \sim \frac{\epsilon}{\delta}, \qquad I_3 \sim \frac{\epsilon}{2(2\delta - \epsilon)}.$$

The general forms of integrals I_4 and I_5 for the above mentioned case $\xi << \xi_R$ are presented in Appendix 1. The integration of the correspondent Feynman integrals in the renormalized two-point correlation function of two surface fields $G^{(0,2)}$ at the first order of the perturbation theory gives for the surface renormalization factors $Z_{\parallel}$ and $Z_{\phi_s^2}$ the following results

$$Z_{\parallel} = 1 + \frac{\bar{v}}{3(1+\epsilon)} + \frac{2\bar{w}I_6}{3}(1 - \frac{I_4}{4I_6}), \tag{33}$$

$$Z_{\phi_s^2} = 1 - \frac{\bar{v}}{3(1+\epsilon)}(1 - 2^{\frac{1+\epsilon}{2}}\,_2F_1[\frac{3-\epsilon}{2}, \frac{\epsilon+1}{2}, \frac{3+\epsilon}{2}, \frac{1}{2}])$$
$$- \frac{2\bar{w}I_6}{3}(1 - \frac{I_4}{4I_6} - 2^{\frac{1+\delta}{2}}\,_2F_1[\frac{3-\delta}{2}, \frac{\delta+1}{2}, \frac{3+\delta}{2}, \frac{1}{2}]), \tag{34}$$

where integrals $I_6 = I_5/(1 + \delta)$ and the function $_2F_1[...]$ is a standard Hypergeometric function.

Combining the renormalization factors $Z_{\parallel}$ and $Z_{\phi_s^2}$ together with the corresponding order of β-functions Eq.(29) the surface critical exponents $\eta_{\parallel}$ and $\eta_{\bar{c}}$ according to (23), (24) can

be obtained

$$\eta_\|(\bar{v}, \bar{w}) = -\frac{\epsilon \bar{v}}{3(1+\epsilon)} - \frac{2}{3}\delta \bar{w} I_6(1 - \frac{I_4}{4I_6}),$$

$$\eta_{\bar{c}}(\bar{v}, \bar{w}) = \frac{\epsilon \bar{v}}{3(1+\epsilon)}(1 - 2^{\frac{1+\epsilon}{2}} {}_2F_1[\frac{3-\epsilon}{2}, \frac{\epsilon+1}{2}, \frac{3+\epsilon}{2}, \frac{1}{2}]) +$$

$$+ \frac{2}{3}\delta \bar{w} I_6(1 - \frac{I_4}{4I_6} - 2^{\frac{1+\delta}{2}} {}_2F_1[\frac{3-\delta}{2}, \frac{\delta+1}{2}, \frac{3+\delta}{2}, \frac{1}{2}]). \tag{35}$$

It should be mentioned that in the case $\xi = 0$ which corresponds to the situation of only surface disorder from Eq.(29) follows that pure bulk fixed point becomes stable.

In the limit $\epsilon \to 0^+$ for the exponent functions $\eta_\|$ and $\eta_{\bar{c}}$ we obtain

$$\lim_{\epsilon \to 0^+} \eta_\| = \lim_{\epsilon \to 0^+} \eta_c \sim -\frac{\tilde{v}}{3} - \frac{2}{3}\tilde{w}\frac{(1-\delta)}{1+\delta}, \tag{36}$$

where the following definitions are introduced: $\tilde{v} = vK_4$ and $\tilde{w} = wK_4$ with $K_4 = 1/(8\pi^2)$. In the case $\epsilon \to 1$ (i.e. $d = 3$) the Eq.(35) lead to

$$\eta_\| = -\frac{\bar{v}}{6} - \frac{2}{3}\bar{w}\frac{(1-\delta)}{1+\delta}(1 - I_7),$$

$$\eta_{\bar{c}} = \frac{\bar{v}}{6}(1 - 4\ln 2) + \frac{2}{3}\bar{w}\frac{(1-\delta)}{1+\delta}(1 - I_7 - 2^{\frac{1+\delta}{2}} {}_2F_1[\frac{3-\delta}{2}, \frac{1+\delta}{2}, \frac{3+\delta}{2}, \frac{1}{2}]), \tag{37}$$

where $I_7 \sim \frac{(1+\delta)}{4\pi^{5/2}}$. In the special case $\delta = 1$, which corresponds to the case of short-range correlated (or random uncorrelated point-like) surface disorder, from (36) and (37) we obtain the surface critical exponents $\eta_\|$ and $\eta_{\bar{c}}$ of the pure model. These results confirm predictions that short-range correlated surface disorder is irrelevant for surface critical behavior and have not any influence on the process of adsorption of polymer chains.

The fixed points $(\bar{v}^*, \bar{w}^*)$ are given by solutions of the system of equations: $\beta_{\bar{v}}(\bar{v}^*, \bar{w}^*) = 0, \beta_{\bar{w}}(\bar{v}^*, \bar{w}^*) = 0$. The stable fixed point is defined as the fixed point where the stability matrix

$$\begin{pmatrix} \frac{\partial \beta_{\bar{v}}}{\partial \bar{v}} & \frac{\partial \beta_{\bar{v}}}{\partial \bar{w}} \\ \frac{\partial \beta_{\bar{w}}}{\partial \bar{v}} & \frac{\partial \beta_{\bar{w}}}{\partial \bar{w}} \end{pmatrix} \tag{38}$$

hold eigenvalues $\lambda_{\bar{v}}$, $\lambda_{\bar{w}}$ with positive real parts. In general, there are three accessible fixed points: the Gaussian (G) fixed point $\bar{v}^* = 0, \bar{w}^* = 0$, the pure (P) SAW fixed point $\bar{v}^* = 3/4, \bar{w}^* = 0$ (here we keep definitions $\bar{v}$ and $\bar{w}$ for rescaled renormalized coupling constant introduced above) and one of two LR mixed fixed points with $\bar{v}_i^* \neq 0, \bar{w}_i^* \neq 0$, where $i = 1, 2$. The Gaussian fixed point with $\lambda_1 = -\epsilon$ and $\lambda_2 = -\delta$ is never stable for positive ϵ and δ. The pure fixed point is stable for systems without disorder and in the case

of positive real parts $\lambda_1 = \epsilon$ and $\lambda_2 = \epsilon/2 - \delta$. When we introduce long-range correlated surface and near the surface disorder into the system one of the LR mixed fixed points, obtained in the framework of (ϵ, δ)- expansion, $\bar{v}^* = \frac{3}{4}\frac{2\delta^2}{\epsilon(\epsilon-\delta)}, \bar{w}^* = \frac{3}{2}\frac{\delta(\epsilon-2\delta)}{\epsilon(\epsilon-\delta)}$ becomes stable for $\delta < \epsilon < 2\delta$ and $a = 3 - \delta < d - 1$.

The above values of the surface critical exponents Eq.(37) $\eta_\parallel$ and $\eta_{\bar{c}}$ formally should be calculated at the above mentioned LR mixed fixed point $(\bar{v}^* \neq 0, \bar{w}^* \neq 0)$.

The other surface critical exponents can be calculated on the basis of the surface scaling relations (see Appendix) and series for the bulk critical exponents ν and η.

In the special case $\delta = 1$ from Eq.(31) and Eq.(35) taking into account Eq.(32)) we obtain the result for critical exponent of pure model [4, 6]. Substituting the above mentioned mixed fixed point $\bar{v}^* \neq 0$ and $\bar{w}^* \neq 0$ into Eq.(31) the first order result for critical exponent ν read:

$$\nu = \frac{1}{2} + \frac{\delta}{8}. \tag{39}$$

This result formally coincides with previous results for the case of long-range correlated bulk disorder (see ([23])), but it should be mentioned that in our case of long-range correlated surface and decaying near the surface disorder the correlation parameter of disorder $a = 3 - \delta$ has another upper critical dimensions and is valid for $a < d - 1$. The correlation parameter δ characterizes long-range correlated disorder in the direction parallel to the surface and parameter ξ describes disorder in the direction perpendicular to the surface. The influence of the exponentially decaying type of disorder in the direction perpendicular to the surface reduces to the renormalization of the coupling constant w_0 via $-w_0\xi = w\mu^\delta$, as was indicated before. In accordance with the complexity of the initial form of the correlation function characterizing disorder (see Eq.(1)), the contributions from parallel and perpendicular part are interconnected which each other and can not be split off. The critical exponent ν describes the overall swelling of the polymer coil and increases when the correlation of the disorder is increased (i.e., $a = 3 - \delta$ decreased).

B. The case of extended disorder $\xi \sim \xi_R$

After performing double (ϵ, δ) - expansion of the above mentioned integrals Eq.(28) and Eq.(30), in the case of extended disorder on the distance of the correlation length ξ_R, i.e. $\xi \sim \xi_R$ we obtain

$$I_2 \sim \frac{\epsilon(1-\delta)}{(1+\delta)}, \qquad I_3 \sim \frac{\epsilon}{3}(1 + \frac{4}{3}(\epsilon - 2\delta)),$$

and

$$I_4 \sim \frac{(\delta - \epsilon)\epsilon}{2\delta\pi^{\frac{d}{2}+1}(1+\delta)}, \qquad I_5 \sim \frac{\epsilon(1-\delta)}{(1+\delta)}. \qquad (40)$$

The general forms of integrals I_4 and I_5 for the present case $\xi \sim \xi_R$ are presented in Appendix 2. In the present case we have the Gaussian (G) fixed point $\bar{v}^* = 0, \bar{w}^* = 0$, the pure (P) SAW fixed point $\bar{v}^* = 3/4, \bar{w}^* = 0$ and two LR mixed fixed points with $\bar{v}_i^* \neq 0, \bar{w}_i^* \neq 0$, where $i = 1, 2$. When we introduce long-range correlated surface and near the surface disorder Eq.(1) with $\xi \sim \xi_R$ into the system one of the LR mixed fixed points $\bar{v}^* = \frac{3}{4}\frac{2\delta}{\epsilon}, \bar{w}^* = \frac{3}{2}\frac{1}{2\epsilon}\sqrt{\frac{3}{8}}(1-\delta)$ becomes stable for $1 < \delta$ and $\epsilon < 4\delta$. Fortunately, in this case $\xi \sim \xi_R$ the LR fixed point is stable in the region where power counting in Eq.(6) shows that such type of disorder is relevant. For the critical exponent ν in this case we obtain

$$\nu = \frac{1}{2} + \frac{\delta}{8}(1 + \frac{1}{2}\sqrt{\frac{3}{8}}). \qquad (41)$$

In the present case of $\xi \sim \xi_R$ the critical exponent ν contains additional contribution proportional to δ in comparison with the case $\xi << \xi_R$. The dependence ν from δ presented in Table 1. As it is easy to see from this table, the values of critical exponent ν increase, when the correlation of the disorder increase (i.e., $a = 3 - \delta$ decrease). The integration of the correspondent Feynman integrals in the renormalized two-point correlation function of two surface fields $G^{(0,2)}$ at the first order of the perturbation theory gives for the surface renormalization factors $Z_{\parallel}$ and $Z_{\phi_s^2}$ in the present case of $\xi \sim \xi_R$ the following results

$$Z_{\parallel} = 1 + \frac{\bar{v}}{3(1+\epsilon)} + \frac{2\bar{w}I_6^*}{3}(1 - \frac{I_4}{4I_6^*}), \qquad (42)$$

$$Z_{\phi_s^2} = 1 - \frac{\bar{v}}{3(1+\epsilon)}(1 - 2^{\frac{1+\epsilon}{2}}{}_2F_1[\frac{3-\epsilon}{2}, \frac{\epsilon+1}{2}, \frac{3+\epsilon}{2}, \frac{1}{2}])$$
$$- \frac{2}{3}\bar{w}I_6(1 - \frac{I_4}{4I_6} - 2^{\frac{1+\delta}{2}}I_9), \qquad (43)$$

where we introduced the next definitions of I_6^*, I_8 and I_9

$$I_6^* = I_6(1 - 2^{\frac{\delta-1}{2}}3^{\frac{1-\delta}{2}}{}_2F_1[\frac{3-\delta}{2}, \frac{1+\delta}{2}, \frac{3+\delta}{2}, -\frac{1}{2}]), \qquad I_8 = \frac{(1+\delta)\Gamma(\delta-1)}{2\Gamma(\delta)},$$

$$I_9 = {}_2F_1[\frac{3-\delta}{2}, \frac{1+\delta}{2}, \frac{3+\delta}{2}, \frac{1}{2}] + \frac{3^{\frac{1-\delta}{2}}}{2}{}_2F_1[\frac{3-\delta}{2}, \frac{1+\delta}{2}, \frac{3+\delta}{2}, -\frac{1}{2}]$$
$$+ I_8(3^{\frac{1-\delta}{2}}{}_2F_1[\frac{3-\delta}{2}, \frac{\delta-1}{2}, \frac{1+\delta}{2}, -\frac{1}{2}] - {}_2F_1[\frac{3-\delta}{2}, \frac{\delta-1}{2}, \frac{1+\delta}{2}, \frac{1}{2}]) \qquad (44)$$

Combining the renormalization factors $Z_\parallel$ and $Z_{\phi_s^2}$ together with the corresponding order of β-functions Eq.(29) the surface critical exponents $\eta_\parallel$ and $\eta_{\bar{c}}$ according to (23), (24) can be obtained

$$\eta_\parallel(\bar{v}, \bar{w}) = -\frac{\epsilon\bar{v}}{3(1+\epsilon)} - \frac{2}{3}\delta\bar{w}I_6^*(1 - \frac{I_4}{4I_6^*}),$$
$$\eta_{\bar{c}}(\bar{v}, \bar{w}) = \frac{\epsilon\bar{v}}{3(1+\epsilon)}(1 - 2^{\frac{1+\epsilon}{2}}{}_2F_1[\frac{3-\epsilon}{2}, \frac{\epsilon+1}{2}, \frac{3+\epsilon}{2}, \frac{1}{2}]) +$$
$$+ \frac{2}{3}\delta\bar{w}I_6(1 - \frac{I_4}{4I_6} - 2^{\frac{1+\delta}{2}}I_9). \qquad (45)$$

In the limit $\epsilon \to 0$ in the present case for the exponent functions $\eta_\parallel$ and η_c we obtain

$$\lim_{\epsilon \to 0} \eta_\parallel = -\frac{\tilde{v}}{3} - \frac{2}{3}\tilde{w}\frac{(1-\delta)}{1+\delta}(1 - 2^{\frac{\delta-1}{2}}3^{\frac{1-\delta}{2}}{}_2F_1[\frac{3-\delta}{2}, \frac{1+\delta}{2}, \frac{3+\delta}{2}, -\frac{1}{2}] - \frac{\delta}{8\pi^3}),$$
$$\lim_{\epsilon \to 0} \eta_c = -\frac{\tilde{v}}{3} + \frac{2}{3}\tilde{w}\frac{(1-\delta)}{(1+\delta)}(1 - 2^{\frac{1+\delta}{2}}I_9 - \frac{\delta}{8\pi^3}), \qquad (46)$$

In the limit case $\epsilon \to 1$ (i.e. $d = 3$) from Eq.(45) we obtain

$$\lim_{\epsilon \to 1} \eta_\parallel = -\frac{\bar{v}}{6} - \frac{2}{3}\bar{w}\frac{(1-\delta)}{(1+\delta)}(1 - 2^{\frac{\delta-1}{2}}3^{\frac{1-\delta}{2}}{}_2F_1[\frac{3-\delta}{2}, \frac{1+\delta}{2}, \frac{3+\delta}{2}, -\frac{1}{2}] - \frac{\delta}{8\pi^2}),$$
$$\lim_{\epsilon \to 1} \eta_c = \frac{\bar{v}}{6}(1 - 4\ln 2) + \frac{2}{3}\tilde{w}\frac{(1-\delta)}{(1+\delta)}(1 - 2^{\frac{1+\delta}{2}}I_9 - \frac{\delta}{8\pi^2}). \qquad (47)$$

In the limit case $\delta \to 1$, which corresponds to the situation of short-range correlated (or random uncorrelated point-like) surface disorder (where $a = 3 - \delta$) from Eqs.(46) and (47) we obtain the surface critical exponents of pure model. The results of calculation of surface critical exponents $\eta_\parallel$ and $\eta_{\bar{c}}$ presented in Table 1. As it is easy to see from this table, the values of surface critical exponent $\eta_\parallel$ and $\eta_{\bar{c}}$ decrease, when the correlation of the disorder increase (i.e., $a = 3 - \delta$ decrease) in comparison with first order results $\eta_\parallel = -0.13$, $\eta_{\bar{c}} = -0.22$ and one-loop order results $\eta_\parallel = -0.204$, $\eta_{\bar{c}} = -0.362$ for pure model without disorder (see [30]).

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V.   SCALING ANALYSIS

The knowledge of the above mentioned surface critical exponents $\eta_\|$ and Φ and bulk critical exponents ν and η is sufficient for the scaling analysis of different characteristics near the multicritical point $1/N \to 0$ and $c \to 0$. So, it allows us to investigate behavior of long-flexible polymer chains near the marginal and adsorbing surface. Furthermore, the crossover from adsorbed to desorbed state can be analyzed.

Let us first consider the mean square end-to-end distance of a chain with one end attached to the surface and the other one freely fluctuating. In the semi-infinite system translational invariance is broken, and the parallel $< R_\|^2 >$ and perpendicular $< R_\perp^2 >$ parts of the average end-to-end distance $< R^2 >=< R_\perp^2 + R_\|^2 >$ should be distinguished. The perpendicular part $< R_\perp^2 >^{1/2}$ in the case $c \geq 0$ is proportional to N^ν and has the same value as the asymptotic behavior in the bulk. In the adsorbed state, $c < 0$, the part $< R_\perp^2 >^{1/2}$ is independent of N and describes the thickness ξ_{th} of the adsorbed chain:

$$\xi_{th} =< R_\perp^2 >^{1/2} \sim \xi_c \qquad c < 0. \tag{48}$$

This thickness diverges for $c = 1/N = 0$, see Eq.(2). According to Eq.(2) this thickness is controlled by the crossover exponent Φ and thus depends crucial of the type of disorder (see Table II). This dependence of the thickness of the adsorbed layer from c for different values of correlation parameter $\delta = 3 - a$ is presented on Figure 2.

The asymptotic scaling form of $< R_\|^2 >^{1/2}$ for $c < 0$ is $< R_\|^2 >^{1/2} \sim |c|^{(\nu^{d-1}-\nu)/\Phi} N^{\nu^{d-1}}$, where ν^{d-1} is the correlation exponent in $d - 1$ dimensions. For $c \geq 0$ the scaling form of $< R_\|^2 >^{1/2}$ is proportional to N^ν, i.e. it is also the same as in the bulk.

As mentioned in Ref. [10], the knowledge of Eqs.(25) and (26) gives access to the short-distance behavior for $l \ll z, r \ll N^\nu$ at the adsorption threshold of the corresponding partition functions with one end fixed and another end free and for the partition function with two ends at the surface

$$Z^\lambda(0, z) \sim z^{a_\lambda} N^{b_\lambda}, \tag{49}$$

$$Z^{\|,\perp}(x) \sim x^{a_{\|,\perp}} N^{b_{\|,\perp}}, \tag{50}$$

where critical exponents are: $a_\lambda = \eta_\| - \eta_\perp$, $b_\lambda = -1 + \gamma_\|$ and $a_{\|,\perp} = 1 - \eta_{\|,\perp} - \Phi/\nu$, $b_{\|,\perp} = -1 - \nu(d - 1) + \Phi$. Table II represents the obtained first order results for the corresponding critical exponents characterizing the process of adsorption of long-flexible

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polymer chains near the adsorption threshold and their dependence from the correlation parameter δ. We note that the values for the cross-over exponent are much smaller than for the case of pure surfaces without any disorder effects. This, however, is compensated by the large values of Flory exponent.

For the fraction of monomers at the surface, N_1/N, the asymptotic behavior is closely related to the crossover exponent [1, 10]:

$$N_1/N \sim \begin{cases} |c|^{(1-\Phi)/\Phi} & \text{if} \quad c < 0 \\ N^{\Phi-1} & \text{if} \quad c = 0 \\ (cN)^{-1} & \text{if} \quad c > 0 \end{cases} . \tag{51}$$

Note that N_1/N displays the signature of the second order adsorption transition for $N \to \infty$ with respect to c. Therefore, N_1/N plays the role of the order parameter of the adsorption transition.

The thickness of the adsorbed chain, ξ_{th}, is closely related to the fraction of monomers at the surface N_1/N [1, 10]. The more monomers are fixed at the wall, the smaller the region occupied by the remaining monomers. In particular, for $c \leq 0$ one obtains using Eqs.(51) and (2) $N_1/N \sim \xi_{th}^{-(1-\Phi)/\nu}$. The first order results of calculations for exponents $(1-\Phi)/\Phi$ and $(1-\Phi)/\nu$ are presented in Table II. The dependence of the fraction of monomers adsorbed at the surface N_1/N on ξ_c for different values δ for $c \leq 0$ (i.e. below the adsorption threshold) is presented in Figure 3.

The knowledge of the above mentioned surface critical exponents give access to the analysis of the scaling behavior of the mean number of the free ends in the layer between z and $z + dz$. The mean number of the free ends in the layer between z and $z + dz$ is proportional to the partition function of a chain with one end fixed at $\mathbf{x}_A = (\mathbf{r}_A, z)$ and the other end free, $Z_N(z)$, where

$$Z_N(z) = \int_0^\infty dz Z_N^\lambda(z', z). \tag{52}$$

Short-distance behavior ($l \ll z \ll \xi_R$) of the $Z_N(z)$ right at the threshold ($c = 0$) is

$$Z_N(z) \sim z^{a'} N^{b'} \tag{53}$$

with $a' = (\gamma - \gamma_1)/\nu$ and $b' = \gamma_1 - 1$. Short-distance behavior ($l \ll z \ll \xi_R$) of the density of monomers in a layer at the distance z from the wall to which one end of the polymer is

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attached, $M_N^\lambda(z)$ right at the threshold ($c = 0$) is

$$M_N^\lambda(z) \sim z^{-\bar{a}} N^{\bar{b}}, \tag{54}$$

where $\bar{a} = 1 - (1 - \Phi)/\nu$, $\bar{b} = -1 + \Phi + \gamma_1$. The exponent $\bar{a}$ has been introduced as the proximal exponent by de Gennes and Pincus [32]. Note that $\Phi > 1 - \nu$ is obtained in all results. Thus, the conjecture by Bouchaud and Vannimenus [33] is obeyed. This means that the adsorption profile is strickly decaying with a positive proximal exponent. The calculation of the dependence of the above mentioned critical exponents a', b' and $\bar{a}, \bar{b}$ from the correlation parameter δ is presented in Table II. The scaling behavior of $Z_N(z)$ and M_N^λ for different values of correlation parameter δ are presented on the Figure 4 and Figure 5, respectively.

VI. CONCLUSIONS

In the present paper we have investigated adsorption on "marginal" and attractive surface of long-flexible polymer chains in media with quenched long-range correlated surface and decaying near the surface disorder of the type (1). The correlation function given in Eq.(1) implies also a layer-like structure of the impurities in the bulk. In such systems the chains has to go around large correlated regions, and effectively occupies a large space, with the defects contained inside the region occupied by the coil and as a result, the polymer chain swells. This explaines the increase of the mean square end-to-end distance and the radius of gyration as a result of the increase of the critical exponent ν (see Table I) when the correlation of the disorder is increased (i.e., $a = 3 - \delta$ is decreased).

If the range of correlation is very large, then the polymer chain may be trapped between the walls of defects. From Fig.4 and Fig.5, Eqs.(53),(54) and results of Tables I,II, we can see that the mean number of free ends in the layer between z and $z + dz$ and the density of monomers in a layer at the distance z from the wall in the near surface region ($l \ll z \ll \xi_R$) both increase for decreasing $a = 3 - \delta$. From the fact that crossover exponent Φ decreases for decreasing a (see Table I) we obtain, that the thickness of the adsorbed layer (see Fig.2) and the fraction of monomers N_1/N as function of ξ_c increase for decreasing a (see Fig.3). From Eq.(51) and results of Table II we obtain that for small values of $|c|$ the fraction of adsorbed monomers N_1/N as function of $|c|$ decreases when the correlation of the disorder

is increased (i.e., $a = 3 - \delta$ is decreased). This indicates that the fraction of the monomers near the wall can be higher then directly at the wall when we add disorder.

Our result in the first order of the (ϵ, δ)-expansion for systems with long range correlated surface and decaying near the surface disorder are in good agreement with our previous results for systems with long-range correlated bulk disorder [24] (also obtained in the framework of the one-loop approximation scheme). We note that the absolute values for surface critical exponents obtained in the framework of (ϵ, δ)-expansion are smaller, than those obtained within the one-loop approximation scheme. A similar situation is found for pure systems without disorder (see results for surface critical exponents $\eta_\parallel$ and η_c obtained with the two different schemes [30]).

The obtained results indicate that the long-range correlated surface and decaying near the surface disorder has influence on the process of adsorption of long-flexible polymer chains on the surface. The system considered in our work belongs to a new universality class. All sets of surface and bulk critical exponents depends from correlation parameter δ of the correlation function describing disorder (see Eq.(1)). As was indicated in [34], performing of the further calculations in the framework of two-loop approximation scheme directly at fixed dimensions $d = 3$ gives possibility to obtain more reliable quantitative results. It will be the subject of forthcoming work.

Appendix 1

The general forms of integrals I_4 and I_5 for the case $\xi << \xi_R$ are:

$$I_4 = \frac{2^{\delta-2}\Gamma[\frac{\delta-\epsilon}{2}](\delta - \epsilon)\pi^{\frac{1-d}{2}}}{\Gamma[\frac{3-\epsilon}{2}]\Gamma[1 - \frac{\delta}{2}]\sin\frac{\pi\delta}{2}\Gamma[\frac{\epsilon}{2}]},$$

$$I_5 = \frac{\Gamma[\frac{\delta}{2}]\Gamma[\frac{3-\delta}{2}]}{\Gamma[\frac{3-\epsilon}{2}]\Gamma[\frac{\epsilon}{2}]}. \tag{1}$$

Appendix 2

The general forms of integrals I_4 and I_5 for the case $\xi \sim \xi_R$ are:

$$I_4 = -\frac{2^{\delta-3}\Gamma[\frac{\delta-\epsilon}{2}](\delta - \epsilon)\pi^{\frac{(1-d)}{2}}}{(1 + \delta)\Gamma[\frac{3-\epsilon}{2}]\sin\frac{\delta\pi}{2}\Gamma[-\frac{\delta}{2}]\Gamma[\frac{\epsilon}{2}]}, \tag{1}$$

$$I_5 = \frac{2^{\frac{1-\delta}{2}}\delta\sqrt{\pi}\Gamma[\delta]\Gamma[\frac{3-\delta}{2}]}{2(1+\delta)\Gamma[\frac{3-\epsilon}{2}]\Gamma[\frac{1+\delta}{2}]\Gamma[\frac{\epsilon}{2}]}{}_2F_1[\frac{5+\delta}{2}, \frac{3-\delta}{2}, \frac{5+\delta}{2}, \frac{1}{2}]. \tag{2}$$

Appendix 3

The individual RG series expansions for the other critical exponents can be derived through standard surface scaling relations [9] with $d = 3$

$$
\begin{aligned}
\eta_\perp &= \frac{\eta + \eta_\parallel}{2}, \\
\beta_1 &= \frac{\nu}{2}(d - 2 + \eta_\parallel), \\
\gamma_{11} &= \nu(1 - \eta_\parallel), \\
\gamma_1 &= \nu(2 - \eta_\perp), \\
\Delta_1 &= \frac{\nu}{2}(d - \eta_\parallel), \\
\delta_1 &= \frac{\Delta}{\beta_1} = \frac{d + 2 - \eta}{d - 2 + \eta_\parallel}, \\
\delta_{11} &= \frac{\Delta_1}{\beta_1} = \frac{d - \eta_\parallel}{d - 2 + \eta_\parallel}\ .
\end{aligned}
\tag{1}
$$

Each of these critical exponents characterizes certain properties of the semi-infinite systems with long-range correlated surface and decaying near the surface disorder, in the vicinity of the critical point. The values ν, η, and $\Delta = \nu(d + 2 - \eta)/2$ are the standard bulk exponents.

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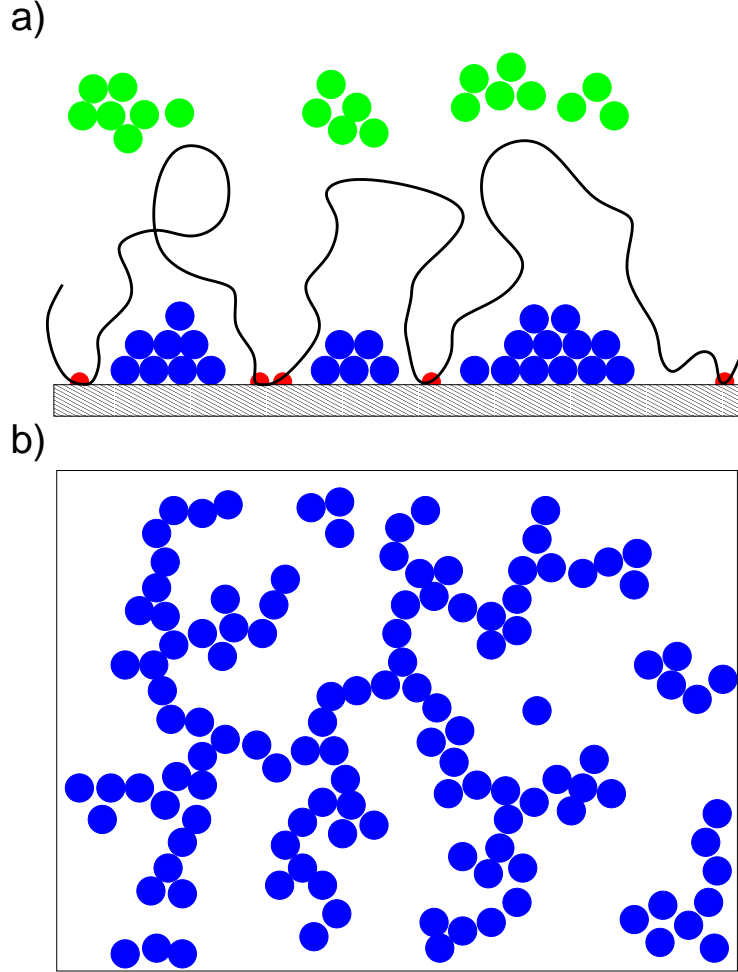[51] M. Shpot, Cond. Mat. Phys. N 10, 143 (1997).

Figures

FIG. 1: Illustration of the type of disorder considered in this work. a) side view: Impurities block parts of the surface for polymer adsorption (blue points) and extent into the bulk (green points). The chain can only adsorb at sites in between the impurities (red points). b) Top view: long range correlated disorder in the direction parallel to the surface is obtained in case of aggregation processes [28] or percolation [29]. Color online only.
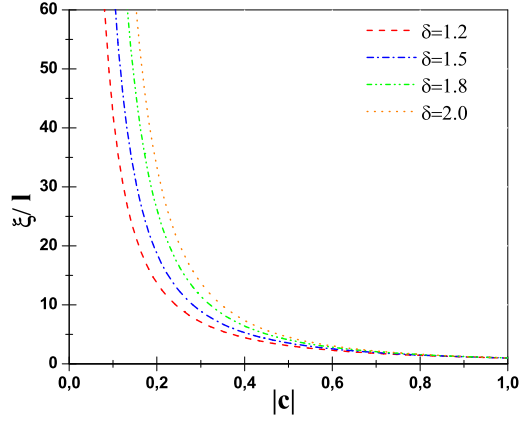
FIG. 2: The dependence of the thickness of the adsorbed layer on c for different values of correlation parameter $\delta = 3 - a$ for $c < 0$(i.e. below the adsorption threshold). Both quantities are dimensionless.
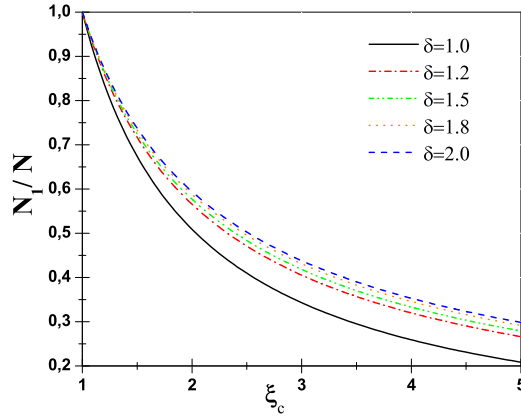

FIG. 3: The dependence of the fraction of monomers at the surface N_1/N on ξ_c for different values δ for $c \leq 0$(i.e. below the adsorption threshold). Both quantities are dimensionless.
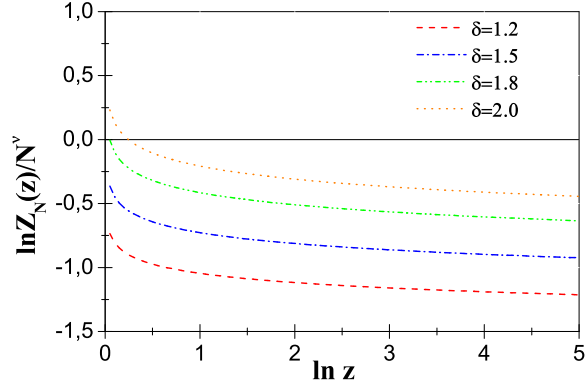
FIG. 4: The partition function $lnZ_N(z)/N^\nu$ just at the adsorption threshold $c = 0$ and for $N = 100$, as a function of lnz for $l \ll z \ll N^\nu$ and for different values of δ.
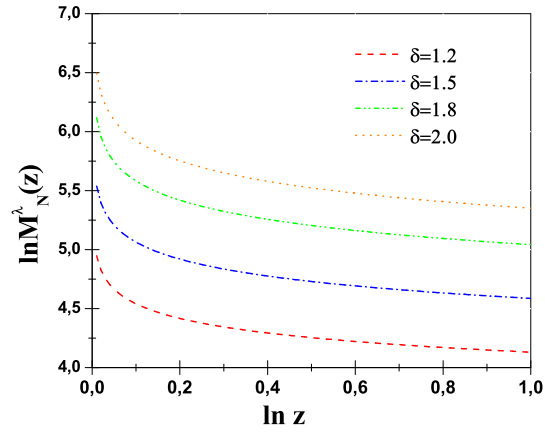

FIG. 5: The density of monomers $lnM_N^\lambda(z)$ in the layer as function of lnz for $l \ll z \ll N^\nu$ just at the adsorption threshold $c = 0$ and for $N = 100$ for different values of δ.

Tables

TABLE I: Bulk and surface critical exponents characterizing the process of adsorption of long-flexible polymer chains at the adsorption threshold $c = c_a$ and in the crossover region between adsorbed and desorbed states calculated for different fixed values of the correlation parameter $\delta = 3 - a$ (in the limit $\epsilon \to 1$).

δ	ν	γ	$\eta_\parallel$	$\eta_\perp$	γ_1	$\gamma_\parallel$	η_c	Φ
1.1	0.680	1.364	-0.271	-0.142	1.430	0.815	-0.492	0.434
1.2	0.696	1.397	-0.295	-0.155	1.469	0.844	-0.536	0.428
1.3	0.712	1.430	-0.320	-0.168	1.508	0.872	-0.581	0.422
1.4	0.729	1.463	-0.345	-0.180	1.547	0.901	-0.626	0.416
1.5	0.745	1.496	-0.369	-0.193	1.587	0.930	-0.671	0.410
1.6	0.761	1.529	-0.394	-0.206	1.626	0.958	-0.715	0.404
1.7	0.778	1.562	-0.418	-0.219	1.665	0.987	-0.760	0.398
1.8	0.794	1.595	-0.443	-0.232	1.704	1.015	-0.805	0.392
1.9	0.810	1.628	-0.468	-0.245	1.743	1.044	-0.849	0.386
2.0	0.827	1.661	-0.492	-0.258	1.782	1.073	-0.894	0.380

TABLE II: Critical exponents characterizing the process of adsorption of long-flexible polymer chains near the adsorption threshold $c = c_a$ calculated for different fixed values of the correlation parameter $\delta = 3 - a$ (in the limit $\epsilon \to 1$).

δ	$\frac{(1-\Phi)}{\nu}$	$\frac{\nu}{\Phi}$	$\frac{(1-\Phi)}{\Phi}$	$\bar{a}$	$\bar{b}$	a'	b'	a_λ	b_λ	$a_\parallel$	$a_\perp$	$b_{\parallel,\perp}$
1.1	0.833	1.567	1.306	0.167	0.864	-0.098	0.430	-0.129	-0.185	0.633	0.504	-2.793
1.2	0.822	1.627	1.338	0.178	0.897	-0.104	0.469	-0.141	-0.156	0.681	0.540	-2.820
1.3	0.812	1.689	1.371	0.188	0.930	-0.111	0.508	-0.153	-0.128	0.728	0.576	-2.846
1.4	0.802	1.753	1.406	0.198	0.963	-0.116	0.547	-0.164	-0.099	0.774	0.610	-2.873
1.5	0.793	1.819	1.441	0.207	0.996	-0.122	0.587	-0.176	-0.071	0.819	0.643	-2.899
1.6	0.784	1.886	1.478	0.216	1.029	-0.127	0.626	-0.188	-0.042	0.864	0.676	-2.926
1.7	0.775	1.956	1.515	0.225	1.062	-0.132	0.665	-0.199	-0.013	0.907	0.708	-2.953
1.8	0.766	2.028	1.554	0.234	1.095	-0.137	0.704	-0.211	0.015	0.950	0.739	-2.979

1.9   0.759 2.102   1.594 0.241 1.128 -0.142 0.743 -0.223   0.044 0.992 0.769 -3.006

2.0   0.751 2.178   1.635 0.249 1.162 -0.147 0.782 -0.234   0.073 1.033 0.799 -3.033